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**(54) PROCESS FOR PRODUCING ALUMINUM-KILLED STEEL FREE OF CLUSTER**

(57) The invention lies in that an alloy of Al and two or more of Ca, Mg and REM is added as a deoxidizing agent to molten steel and  $Al_2O_3$  in the resulting inclusion is adjusted to a range of 30-85 wt% to obtain alumina cluster-free Al-killed steel.

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## Description

## TECHNICAL FIELD

5 This invention relates to a method of producing Al-killed steel for obtaining defect-less and clean steel product by deoxidizing molten steel without producing alumina cluster.

## BACKGROUND ART

10 In general, in case of the production of Al-killed steel, pig iron is decarburized and refined in a converter and tapped into a ladle, which is deoxidized with Al to remove oxygen in molten steel as an oxide and adjusted to proper composition and then continuously cast to obtain a cast slab.

15 In the above deoxidation with Al, there is taken a means for aggregating and coalescing the oxide through gas agitation or in a RH degassing device to promote the floating of the oxide, but the oxide or alumina inevitably remains in the cast slab.

Such an alumina is liable to form cluster. Particularly, when the cluster is caught in a surface layer portion of the cast slab, a surface quality of an extremely-thin steel sheet product such as steel sheet for automobile requiring a beauty appearance is damaged. In this type of the steel sheet, therefore, it is very important to prevent the occurrence of alumina cluster.

20 As a means of deoxidizing steel for preventing the formation of alumina cluster, there has hitherto been proposed and disclosed a method of subjecting molten steel (high-carbon steel) to composite deoxidation treatment with an alloying agent consisting of Ca: 10-30%, Al: 2-20%, Mg: 1-15%, Si: 10-60%, Ba: 10-30% and the balance of Fe in, for example, JP-A-51-5224 (method of producing high-cleaned steel).

25 However, such an alloying agent contains Ba, so that when it is added to molten steel as a deoxidizing agent, there is a problem in the maintenance of working environment. And also, it contains 10-60% of Si, so that Si remains in molten steel. For this end, it can not be used in the steel sheet for automobile requiring a severe work. Further, when the above alloying agent is used, Ca and Mg having a high steam pressure are added in relatively greater amounts, so that the yield after the addition to molten steel becomes not constant. Therefore, the formation of composite inclusion from alumina cluster and the shape controllability of the inclusion become unstable, so that the effect of preventing the formation of alumina cluster becomes variable.

30 In JP-A-54-116312 (deoxidizing alloy for molten steel) is proposed and disclosed a deoxidizing alloy for molten steel containing 2-10 mol% of one or more elements of Group IIIa (Y, Ce, La and so on) to Al.

35 However, when deoxidation is carried out by using such a deoxidizing alloy for molten steel, it is effective to prevent the formation of dendritic oxide inclusion and the prevention effect for big cluster is observed, but it is insufficient to reduce cluster having a diameter of about 100  $\mu\text{m}$ , which comes into problem in the steel sheet for automobile, and also there is a problem that the floating and separating properties of the resulting oxide inclusion are poor.

## DISCLOSURE OF INVENTION

40 The invention is to advantageously solve the aforementioned problems and to propose a method of producing clean Al-killed steel having no alumina cluster and less defect.

The inventors have made experiments and investigations for solving the problems of the above conventional techniques and as a result the invention has been accomplished. The constructions of the invention advantageously achieving the invention are as follows.

45 1. A method of producing cluster-free Al-killed steel containing sol. Al: not less than 0.005 wt%, which comprises charging an alloy consisting of Al and two or more elements selected from Ca, Mg and REM into molten steel to conduct deoxidation and adjust  $\text{Al}_2\text{O}_3$  in the resulting inclusion to a range of 30-85 wt% (first invention).

50 2. A method of producing cluster-free Al-killed steel according to the first invention, wherein a composition of the alloy satisfies a relation of the following equation (1) (second invention):

$$[\text{Ca}(\text{wt}\%) + \text{Mg}(\text{wt}\%) + \text{REM}(\text{wt}\%)]/\text{Al}(\text{wt}\%) \leq 0.5 \quad (1)$$

55 3. A method of producing cluster-free Al-killed steel according to the first invention, wherein a composition of the alloy satisfies a relation of the following equations (2) and (3) (third invention):

$$[\text{Ca}(\text{wt}\%) + \text{Mg}(\text{wt}\%)]/\text{Al}(\text{wt}\%) \leq 0.3 \quad (2)$$

$$\text{REM}(\text{wt}\%)/\text{Al}(\text{wt}\%) \leq 0.1$$

(3)

4. A method of producing cluster-free Al-killed steel according to the first, second or third invention, wherein molten steel is subjected to a preliminary deoxidation so as to provide free oxygen in molten steel of not more than 200 wtpm (fourth invention).

The function and effect of the invention will be described below.

At first, the reason why the invention restricts to Al-killed steel containing not less than 0.005 wt% of sol. Al is due to the fact that when the amount of sol. Al is less than 0.005 wt%, Al forms a composite inclusion with alloying components included in molten steel such as Si, Mn and the like and hence alumina cluster hardly occurs and the application of the invention is not particularly necessary.

Then, the invention will be described with respect to the deoxidizing agent of alloy.

The alloy used as a deoxidizing agent is an alloy of Al and two or more of Ca, Mg and REM (Ce, La and the like) obtained by previously melting and homogenizing them.

The reason why the deoxidizing agent is the alloy of Al and two or more of Ca, Mg and REM is due to the fact that when it is an alloy of Al and one of Ca, Mg and REM, the formation of composite inclusion and the shape control thereof become unstable and the effect of preventing the formation of alumina cluster is insufficient and hence the effect of satisfactorily improving the surface quality in the thin steel sheet can not be achieved.

In Fig. 1 is shown a graph showing a relation between a concentration of a metallic element (Ce, Ca, Mg, Al, Si) at a temperature of 1600°C and an oxygen activity ( $a_O$ ).

In Fig. 1, for example, when an activity of  $\text{Al}_2\text{O}_3$  is 0.5, an activity of CaO is 0.2 and an activity of  $\text{Ce}_2\text{O}_3$  is 0.2 in a low melting point composite inclusion forming no aimed alumina cluster, if Al in molten steel is 150 wtpm, equivalent Ca and Ce are 6 wtpm and 3 wtpm, respectively. Such compositions of molten steel and composite inclusion are obtained by deoxidizing with a small amount of Mg-REM-Al alloy.

Further, when an activity of  $\text{Al}_2\text{O}_3$  is 0.5, an activity of MgO is 0.2 and an activity of  $\text{Ce}_2\text{O}_3$  is 0.2 in the aimed composite inclusion, if Al in molten steel is 150 wtpm, equivalent Mg and Ce are 12 wtpm and 3 wtpm, respectively. Such compositions of molten steel and composite inclusion are obtained by deoxidizing with a small amount of Mg-REM-Al alloy.

The composition of the alloy as the deoxidizing agent is favorable to be that a value of  $(\text{Ca}+\text{Mg}+\text{REM})/\text{Al}$  represented by wt% is not more than 0.5.

When the value exceeds 0.5, the desired inclusion composition is not obtained. When greater amounts of CaO and MgO are included in the composition of the inclusion, if they appear at the surface of the product, there may be caused a problem of generating rust. On the other hand, when a greater amount of REM oxide is included, the shape of the resulting inclusion becomes square and the degree of controlling the formation of cluster is insufficient.

Preferably, the alloy has a composition that a value of  $(\text{Ca}+\text{Mg})/\text{Al}$  is not more than 0.3 and a value of  $\text{REM}/\text{Al}$  is not more than 0.1, and it is possible to relatively easily obtain a desired composition of the composite inclusion by the addition at once. When the value of  $(\text{Ca}+\text{Mg})/\text{Al}$  exceeds 0.3, not only the increase of the above rust generation is brought about but also the cost of the alloying agent becomes high. When the value of  $\text{REM}/\text{Al}$  exceeds 0.1, individual sulfide and oxide of REM are apt to be produced owing to strong deoxidation and desulfurization abilities of REM. Such sulfide and oxide of REM are large in the specific gravity, so that it is difficult to separate and remove them from molten steel.

In the invention, it is important to adjust the concentration of  $\text{Al}_2\text{O}_3$  in the resulting composite inclusion to a range of 30-85 wt%. Preferably, the  $\text{Al}_2\text{O}_3$  concentration is within a range of 30-70 wt%.

This is due to the fact that when the  $\text{Al}_2\text{O}_3$  concentration is less than 30 wt% or exceeds 85 wt%, the effect aiming at the invention is not obtained and the melting point of the composite inclusion (oxide inclusion) produced even in both cases becomes higher and hence the surface quality in the thin steel sheet is not improved.

In addition, when the  $\text{Al}_2\text{O}_3$  concentration in the composite inclusion is less than 30 wt%, the amounts of CaO and MgO become relatively large. If the composite inclusion having such a composition is existent in molten steel, it may result in the rust generation at the thin steel sheet. When the  $\text{Al}_2\text{O}_3$  concentration exceeds 85 wt%, there are problems that nozzle clogging in the casting and occurrence of sliver flaw in the thin steel sheet can not be prevented and the like.

When the  $\text{Al}_2\text{O}_3$  concentration is not more than 70 wt%, the effect of preventing cluster becomes more stable and the effect of improving the surface quality is remarkable. Therefore, the preferable  $\text{Al}_2\text{O}_3$  concentration is not more than 70 wt%.

Further, the composite inclusion has a more preferable composition that the  $\text{Al}_2\text{O}_3$  concentration is within a range of 30-85 wt% and a value of  $(\text{CaO}+\text{MgO})/\text{Al}_2\text{O}_3$  by weight ratio is within a range of 0.5-0.8.

In the invention, the alloy used as the deoxidizing agent is expensive as compared with Al, so that it is desirable to reduce the addition amount within a range capable of adjusting the composition of the composite inclusion. For this purpose, it is very effective to preliminarily deoxidize a concentration of free oxygen in molten steel to not more than 200 wtpm prior to the addition of the alloy from a viewpoint of economical reasons. Such a preliminary deoxidation may be

carried out by agitation of molten steel under vacuum, deoxidation with C, light deoxidation with Al, deoxidation with Si or FeSi or the like, which does not affect the effect of the invention.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relation between a concentration of a metallic element at a temperature of 1600°C and an oxygen activity; and

Fig. 2 is a photograph of a metal structure showing a shape of an inclusion, wherein (a) is a case of deoxidizing with an alloy and (b) is a case of deoxidizing with Al.

## BEST MODE FOR CARRYING OUT THE INVENTION

### Example 1

Molten steel containing C: 0.01 wt%, Si: tr, Mn: 0.2 wt%, P: 0.010 wt% and S: 0.010 wt% was prepared in a high frequency melting furnace of 30 kg in capacity and carbon particles were added to conduct preliminary deoxidation while being held at a temperature of 1600°C, whereby molten steel having free oxygen: 130 wtpm was obtained.

After molten steel was deoxidized by adding 0.8 kg/t of 79 wt% Al-16 wt% Ca-5 wt% REM alloy, it was cast to obtain a steel ingot containing C: 0.02 wt%, Si: tr, Mn: 0.2 wt%, P: 0.010 wt% and S: 0.010 wt%.

A photograph of a metal structure showing a shape of an inclusion in the thus obtained steel ingot is shown in Fig. 2(a) together with a photograph of Fig. 2(b) through usual deoxidation with only Al as a comparison.

As seen from Fig. 2, (a) based on the above deoxidation with the alloy has no cluster as seen in (b) based on the deoxidation with Al but spherical composite inclusion is formed therein.

### Example 2

Molten steel having free oxygen: 180 wtpm was prepared by preliminary deoxidation after molten steel having the same composition as in Example 1 was prepared in the same melting furnace as in Example 1. After the thus obtained molten steel was deoxidized by adding 0.6 kg/t of 78 wt% Al-15 wt% Mg-7 wt% REM alloy, it was cast to obtain a steel ingot having substantially the same composition as in Example 1.

As a result of investigating the inclusion in the thus obtained steel ingot, all inclusions were spherical and had a composite composition of  $\text{MgO-Al}_2\text{O}_3\text{-Ce}_2\text{O}_3$ .

### Example 3

Molten steel containing C: 0.03 wt%, Si: tr, Mn: 0.02 wt%, P: 0.015 wt% and S: 0.010 wt% was prepared in a top-and bottom-blown converter of 280 t.

After decarburization treatment was carried out by refluxing molten steel in a RH degassing device, preliminary deoxidation was conducted by using 0.7 kg/t of metallic Al. In this case, the temperature of molten steel before the treatment was 1605°C, and free oxygen in molten steel lowered from 600 wtpm to 180 wtpm for the refluxing time of 5 minutes. A total oxygen in molten steel was 190 wtpm after the treatment. And also, C was 18 wtpm.

Thereafter, molten steel was added with 0.8 kg/t of 79% Al-10% Ca-6% Mg-5% REM alloy and subjected to a refluxing treatment for 10 minutes.

The temperature of molten steel after the treatment was 1585°C and total oxygen in molten steel was 18 ppm.

The thus obtained molten steel of Al-alloy killed steel was poured into a continuously casting mold of 220 × 1200 mm through a tundish and cast at a casting rate of 2.0 m/min to obtain a cast slab. This cast slab was heated and subjected to hot rolling and cold rolling to obtain a cold rolled steel sheet having a thickness of 0.8 mm and then a reject rate of surface defect was measured.

As a result, the reject rate of surface defect (weight ratio) in the conventional single Al-killed steel was 0.8%, while the reject rate of surface defect in the above obtained cold rolled steel sheet was 0%. And also, the inclusion in the cold rolled steel sheet had the  $\text{Al}_2\text{O}_3$  concentration of 30-70.

Thus, the Al-killed cold rolled steel sheet produced by the invention had no alumina cluster and was very excellent in the surface quality and had no surface defect resulted from the inclusion.

## INDUSTRIAL APPLICABILITY

In the production of Al-killed steel according to the invention, an alloy of Al and two or more elements selected from Ca, Mg and REM is used as a deoxidizing agent and the concentration of  $\text{Al}_2\text{O}_3$  in the resulting inclusion is adjusted to

a range of 30-85 wt%.

According to the invention, there can be produced alumina cluster-free Al-killed steel and it is possible to previously prevent the occurrence of defect resulted from alumina cluster as a drawback in the Al-killed steel. Furthermore, the Al-killed steel produced by the invention is advantageously applicable in not only thin steel sheet for automobile but also high-carbon steels for bearing or spring, steel for thick plate or pipe, stainless steel and the like.

# Claims

1. A method of producing cluster-free Al-killed steel containing sol. Al: not less than 0.005 wt%, which comprises charging an alloy consisting of Al and two or more elements selected from Ca, Mg and REM into molten steel to conduct deoxidation and adjust  $Al_2O_3$  in the resulting inclusion to a range of 30-85 wt%.

2. A method of producing cluster-free Al-killed steel according to claim 1, wherein a composition of the alloy satisfies a relation of the following equation (1):

$$[Ca(wt\%) + Mg(wt\%) + REM(wt\%)]/Al(wt\%) \leq 0.5 \quad (1)$$

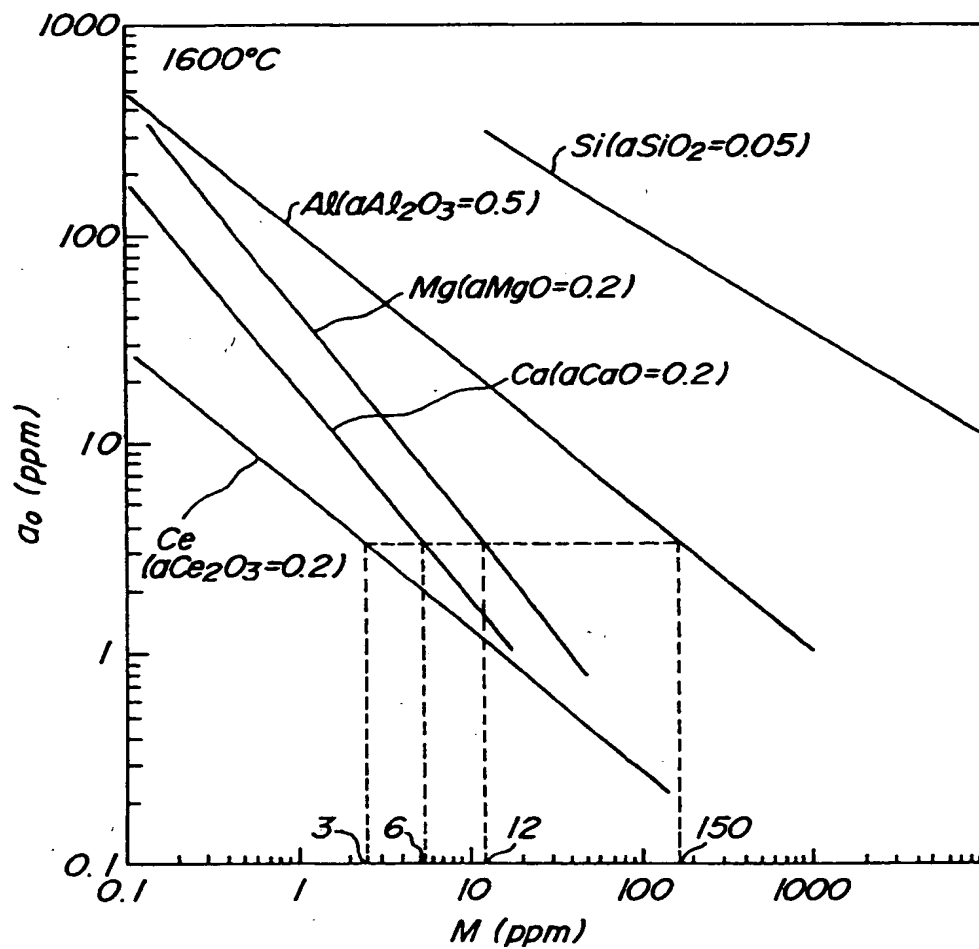
3. A method of producing cluster-free Al-killed steel according to claim 1, wherein a composition of the alloy satisfies a relation of the following equations (2) and (3):

$$[Ca(wt\%) + Mg(wt\%)]/Al(wt\%) \leq 0.3 \quad (2)$$

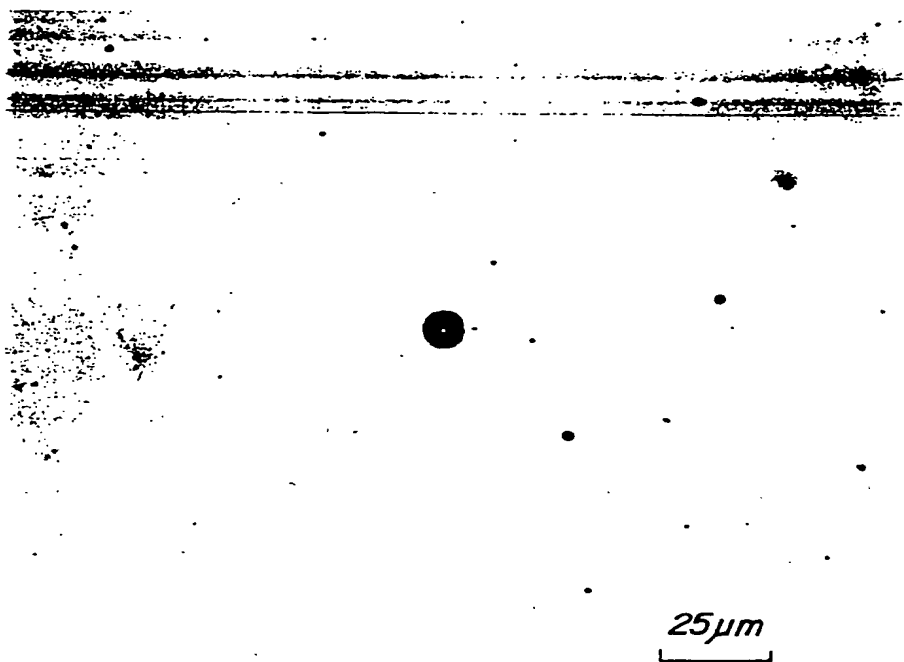
$$REM(wt\%)/Al(wt\%) \leq 0.1 \quad (3)$$

4. A method of producing cluster-free Al-killed steel according to any one of claims 1-3, wherein molten steel is subjected to a preliminary deoxidation so as to provide free oxygen in molten steel of not more than 200 wtpm.

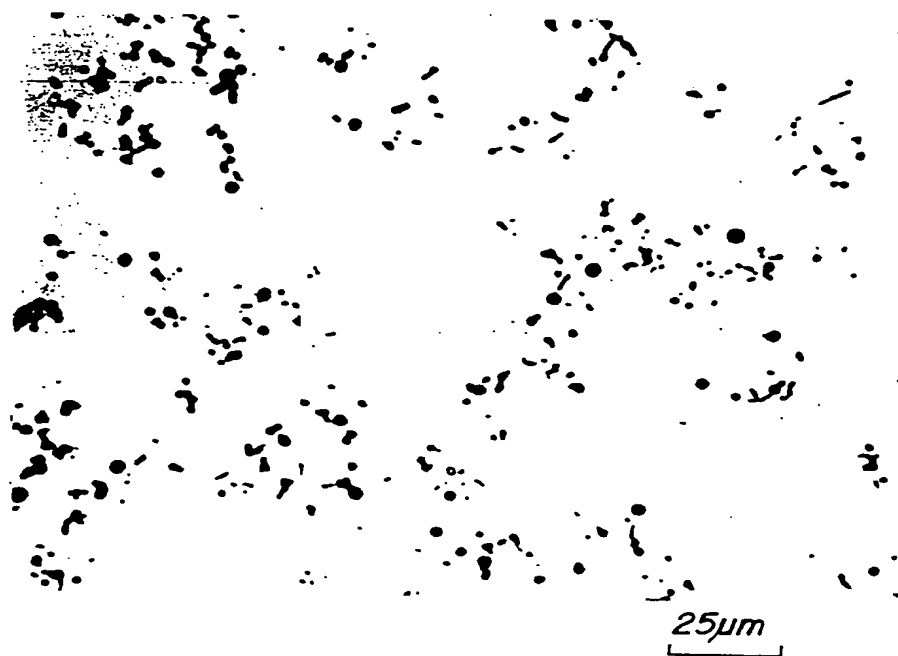
FIG. 1



**FIG. 2** (a)



(b)



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/00989

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>6</sup> C21C7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup> C21C7/06, C21C7/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996	Jitsuyo Shinan Toroku
Kokai Jitsuyo Shinan Koho	1971 - 1997	Koho
Toroku Jitsuyo Shinan Koho	1994 - 1997	1996 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 1-36527, B2 (Japan Casting Co., Ltd.), August 1, 1989 (01. 08. 89), Table 3 (Family: none)	1, 2, 4
Y	JP, 49-26413, B1 (Nippon Steel Corp.), July 9, 1974 (09. 07. 74), Column 2, lines 5 to 16 (Family: none)	1, 2, 4
Y	JP, 52-3328, B2 (Kawasaki Steel Corp.), January 27, 1977 (27. 01. 77), Claim (Family: none)	4
A	JP, 62-7816, A (Nippon Steel Corp.), January 14, 1987 (14. 01. 87) (Family: none)	1 - 4
A	JP, 54-116312, A (Director General of National Research Institute for Science and Technology Agency), September 10, 1979 (10. 09. 79) & US, 4289533	1 - 4

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

June 16, 1997 (16. 06. 97)

Date of mailing of the international search report

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Name and mailing address of the ISA/

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/00989

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 52-59014 (Hitachi Cable, Ltd.), May 16, 1977 (16. 05. 77) (Family: none)	1 - 4

Form PCT/ISA/210 (continuation of second sheet) (July 1992)